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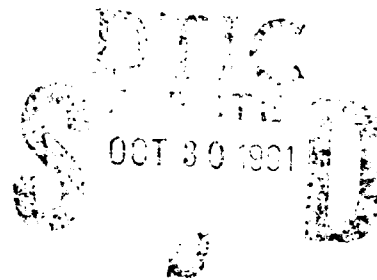
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NOVEL VACUUM BAG PROCESSING APPROACHES TO VOID REDUCTION IN CARBON/EPOXY COMPOSITES

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ABSTRACT

Several novel void reduction techniques were investigated in this study. They are vibration-assisted vacuum composite processing (VAVCP), porous scrim layering (PSL), microporous membrane processing (MMP), and Narmco Materials, Inc.'s Thick Laminate Prepreg (TLP). In VAVCP, low frequency vibration was applied during the pregelation period of the cure cycle of vacuum bag processed carbon/epoxy laminates. This process affected only established gas bubbles. Decreased void content in excess of 50% and increased laminate densification of 0.8% were measured. Data also indicated an approximate 10% increase in size of the remaining voids. The PSL process had no detectable effect on void content; it was ineffective in removing voids. MMP showed the ability to remove volatile water vapor from within the preform interior. Narmco's TLP lowered void content of vacuum bag processed laminates by 50%. Volatile gas and mechanically entrapped gas bubbles respond to different methods of removal from the preform interior. To achieve a near-void-free vacuum bag processed laminate, each form of entrapped gas needs to be addressed separately; a hybrid gas removal process is needed. This process would consist of a combination of in-process gas removal methods: one targeted for established voids; e.g., VAVCP and TLP, and a second targeted for dissolved volatile gases; e.g., TLP and MMP.

NOMENCLATURE

Throughout this report the terms void content, void volume fraction, and the symbol v_v are interchangeable.

DEFINITION OF SYMBOLS

W_c	composite weight
W_{fc}	carbon fiber weight
W_{fs}	scrim fiber weight
W_m	matrix weight
K_{fc}	correction factor for carbon fiber weight due to acid reaction
ρ_e	experimentally measured composite density
ρ_t	theoretical density of the composite, i.e., density assuming no voids present
ρ_{fc}	manufacturer quality assurance data for carbon fiber density
ρ_{fs}	manufacturer quality assurance data for scrim fiber density
ρ_m	manufacturer quality assurance data for matrix density
v_f	fiber volume fraction (including scrim)
v_m	matrix volume fraction
v_v	void volume fraction
σ	σ_{n-1} standard deviation



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INTRODUCTION

Vacuum bag and autoclave cure methods for fabricating reproducible quality polymer composites are well established and standardized. As this field of composites processing continues to mature, the thrust of developmental work naturally shifts to areas of need. One current thrust area is an expanding effort to develop more cost effective processing methods that do not sacrifice part quality. One area of exploration has been a search for new methods which would eliminate the need for costly autoclave processing. Investigations on non-autoclave processing have been conducted and several methods have been developed with reported success¹⁻⁵ but have not been proven enough to be embraced by manufacturers who already have reliable autoclave production methods in place.

Vacuum bag and autoclave composite processing are very similar fabrication methods. Both are open mold processes which act on a composite preform inside an evacuated bag, the interior of which is arranged to maintain easy gas flow from the preform to an attached external vacuum source. Another shared and required aspect of both processes is the use of external hydrostatic pressure to compress and consolidate the preform prior to matrix gelation. It is in the degree of this external pressure that the two methods differ. In an autoclave chamber it is easy to attain and control much higher pressures than in a simple vacuum bag molding. These features have made autoclave processing a workhorse in the advanced composite manufacturing industry. The reason for this wide acceptance is that part quality is increased by the high external pressure; void content drops substantially while fiber content rises.

This is not to say that vacuum bag processing is not useful. It is a pragmatic process which is widely used to fabricate composite end items which are not critically dependent upon low void volume or high fiber volume. There are many applications of this sort such as ground vehicle components, secondary structural members, and more rudimentary composite end items.

Drawbacks of autoclave processing are high initial investment cost and the hazards associated with the high pressure, especially when large scale autoclaves are used. Vacuum bag processing, on the other hand, is more economical and less hazardous. These reasons make developing nonautoclave technology an important goal.

In polymer composite processing voids inevitably occur. The degree of concern over void content in a composite part depends largely upon its application. In many composite applications void content is quite critical, and levels above about 1.5% are unacceptable such as in advanced composite dynamic aerospace structures like helicopters. In other applications levels of 6% and higher can be tolerated.

Clear relationships between void content and composite properties have been established.^{6,7} In general, voids are an undesirable material defect which should be minimized or eliminated

1. DAVE, R., KARDOS, J. L., CHOI, S. J., and DUDUKOVIC, M. P. *Autoclave Versus Non-autoclave Composite Processing*. Proc. 32nd Int. SAMPE Symp., Anaheim, CA, April 1987, p. 325.
2. MATIENZO, L. J., SHAH, T. K., and VENABLES, J. D. *Viewing Glass Experiments: A New Technique to Study the Curing of Composite Laminates*. Proc. 30th Nat. SAMPE Symp., Anaheim, CA, March 1985, p. 330.
3. NEWSAM, S. M. *Vacuum Moulding of High Quality Carbon Reinforced Composite Components*. Proc. SAMPE Eur. Chptr. 3rd Tech. Mtg., Paper 26, London, U. K., March 1983.
4. SEIL, C. A., and LIVELY, G. W. U. S. Patent 3,405,019. *Vacuum Bonding Process*. October 8, 1968.
5. MCGANN, T. W., and OLSEN, W. G. U. S. Patent 4,357,193. *Method of Fabricating a Composite Structure*. November 2, 1982.
6. JUDD, N. C. W., and WRIGHT, W. W. *Voids and Their Effects on the Mechanical Properties of Composites - An Appraisal*. SAMPE J., v. 14, no. 1, 1978, p. 10.
7. YOKOTA, M. J. *In Process Controlled Curing of Resin Matrix Composites*. SAMPE J., v. 14, no. 4, 1978, p. 11.

whenever reasonably possible. Their presence in the matrix is particularly detrimental to inter-laminar shear strength and fatigue life.

A study of two novel void reduction methods for processing carbon/epoxy composites has been made. These methods are vibration-assisted vacuum composite processing (VAVCP) and porous scrim layering (PSL). The VAVCP results presented here have been reported previously.⁸ This study also investigates the finding of Matienzo, et al.² and of Newsam³ who have reported using microporous membrane processing to attain low void content in carbon/epoxy high quality composite laminates using vacuum compaction as the sole means of consolidating pressure. Lastly, this study investigates a product developed by Narmco Materials, Inc. called Thick Laminate Prepreg (TLP). This product was developed to lower void levels in autoclave processed thick epoxy-matrix laminates.^{9,10}

EXPERIMENTAL

Processing Methods

The composites used in this study were both carbon fiber reinforced polymer epoxy prepreps; Hercules AS4/3501-6 and Narmco T300/5208. The 3501-6 and the 5208 are comparable resin systems. Their composition and properties are quite similar and are both widely used in commercial production. Test groups of (0/90)_{4s} laminates were fabricated. The (0/90)_{4s} sequence was chosen for two reasons: it is a motion-inhibiting environment in which to analyze void migration, and is also a commonly occurring sequence in the design of composites. All preforms were laid up and vacuum bagged on a release-coated aluminum tool plate and the assemblies placed in an air circulating oven or autoclave. All test groups had an aluminum caul plate placed over the top surface during processing except for the microporous membrane processing (MMP) group which had a microporous membrane covering the top surface. Table 1 shows the test approach used to study the void reduction processes. Figure 1 shows the standard cure cycle used in processing both the 3501-6 and 5208 epoxy resin systems. (This is one of several industry standard cure cycles commonly used to cure both of these resin systems.)

Table 1. MATRIX USED TO STUDY VOID REDUCTION PROCESSING METHODS

Process	Preliminary Screening Runs	Main Round Processing
VAVCP	N/A	(0/90) _{4s}
PSL	1. Nonwoven Carbon Mat 2. Open Mesh Glass Style 1643 3. Plain Woven Glass Style 104 4. Plain Woven Glass Style 3733	$\left[(0/90)_4, \left(\begin{array}{c} \text{Style 104} \\ \text{Scrim Layer} \end{array} \right), (90/0)_4 \right]$
MMP	N/A	(0/90) _{4s}
TLP	N/A	(0/90) _{4s} Autoclave Cure (0/90) _{4s} (0/90) ₇₅ Autoclave Cure

*All process groups were vacuum bag cured unless otherwise noted.

8. GHIORSE, S. R., and JURTA, R. M. *Effects of Low Frequency Vibration Processing on Carbon/Epoxy Laminates*. Composites, v. 22, no. 1, 1991, p. 3.
9. THORFINSON, B., and BIERMANN, T. F. *Production of Void Free Composite Parts Without Debulking*. Proc. 31st Int. SAMPE Symp., April 1986, p. 480.
10. THORFINSON, B., and BIERMANN, T. F. *Degree of Impregnation of Prepregs - Effects on Porosity*. Proc. 32nd Int. SAMPE Symp., April 1987, p. 1500.

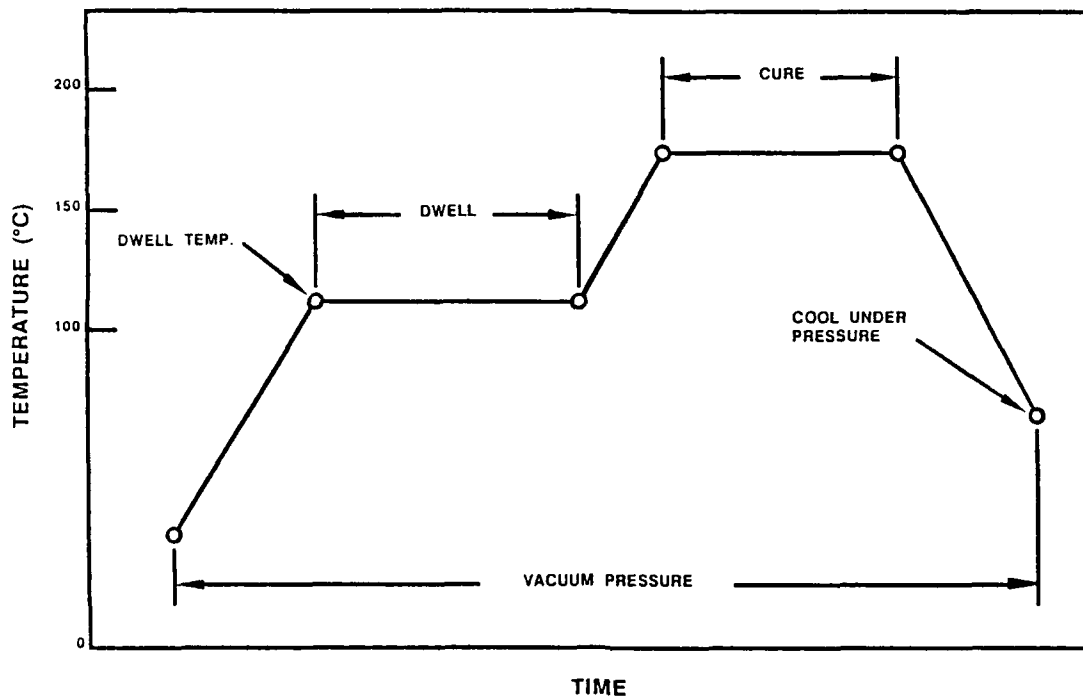


Figure 1. Cure cycle used to process the (0/90)_{4s} laminates.

Vibration-Assisted Vacuum Composite Processing

VAVCP, as shown in Figures 2 and 3, utilizes a simple air driven mechanical shaker table; i.e., a rotating imbalance secured to the tool plate mounted on rubber pads. Low frequency vibration was specifically targeted over higher frequencies approaching ultrasonic. It was felt that success might be achieved in this range and that follow on technology transfer would be relatively quick and inexpensive. Hercules AS4/3501-6 prepreg was used to study this process. The aim of this approach was to impart kinetic energy to establish entrapped gas bubbles, allowing them to overcome potential energy barriers encountered as they are driven by a light pressure gradient to migrate along interior lamina planes, through the viscous resin, and exit at the preform edges. The vibratory frequency was not monitored, nor was its amplitude, but control of the frequency was able to be contained between 30 Hz and 100 Hz (the frequency fluctuated between these limits due to air supply variation). The VAVCP preforms were vacuum bagged onto the release-coated vibrating tool plate. The assembly was placed inside an air circulating oven. The shaker was run from the start of the cure cycle until 30 minutes after the preform core temperature reached 175°C, well after resin gelation. The shaker was then stopped and the cure cycle completed with the tool plate static.

Porous Scrim Laying

In the PSL study, various scrim styles were chosen on the basis of tradeoffs between ease of gas removal, laminate integrity, and the amount of available excess resin in the Hercules AS4/3501-6 prepreg.

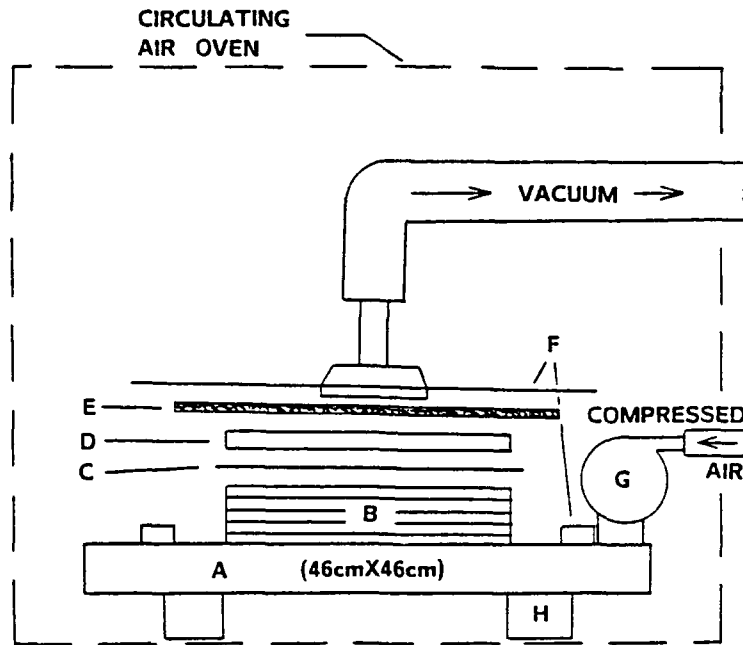


Figure 2. Tooling and layup for the VAVCP process; a) aluminum tool plate, c) release film, e) breather cloth, g) vibrator, b) carbon/epoxy preform, d) aluminum caul plate, f) vacuum bag and sealant, h) rubber mounts.

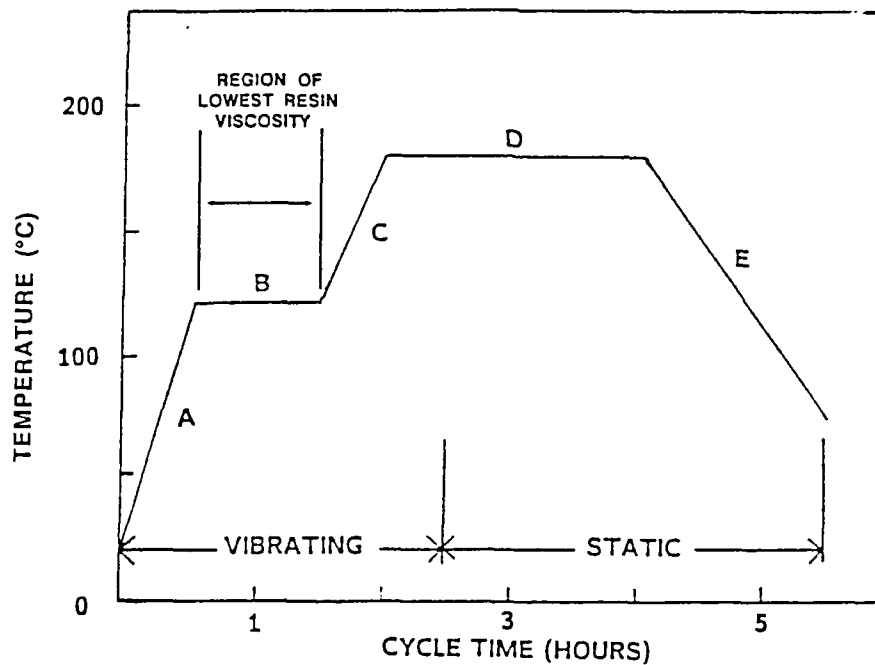


Figure 3. Vacuum cure cycle for the VAVCP process.

- a) Ramp to 120°C
- b) One hour dwell at 120°C
- c) Ramp to 180°C
- d) Two hour dwell at 180°C (vibration off after one half hour)
- e) 90 minute cooldown ramp

Laying up a porous scrim preform does not differ much from standard prepreg lay up procedure. Twelve inch squares of prepreg were laminated on a tool plate. A larger 13 inch square dry scrim layer was placed at the center of the preform. The lay up was then completed in the usual manner, making sure the exposed scrim layer edges overlapped the breather cloth around the entire perimeter of the preform. This lay up scheme attempts to establish a thin, dry, porous evacuated layer giving interior entrapped gases an avenue to quickly exit the laminate prior to matrix gelation.

Microporous Membrane Processing

Dissolved gas diffusion through a viscous fluid is a slow process, especially when the driving pressure gradient is small, as is the case within a vacuum-bagged preform. In MMP, a microporous Teflon* membrane (Garlock, Inc.) was placed over the entire top surface of each preform. Hercules AS4/3501-6 prepreg was used. The membrane, with pores on the order of two micrometers diameter, creates a large porous surface area that reportedly allows diffusing gases to exit the preform.^{2,3} At the same time, because the pores are so minute, the membrane acts as a solid barrier film to the liquid resin. Substantially lower void contents using this process have been reported.^{2,3} A 120°C degassing dwell temperature was used for this processing. The staging dwell time was varied from 30 minutes to six hours. Figures 4 and 5 show the 3501-6 epoxy resin viscosity behavior during this time span at 120°C.¹¹

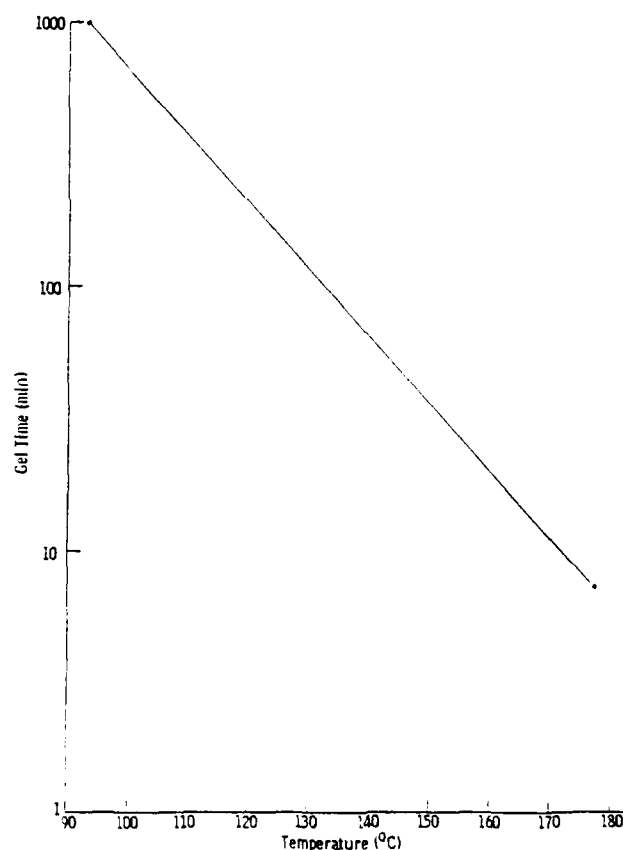


Figure 4. Gel curve of the Hercules 3501-6 epoxy resin (from Hercules Fibers, Inc. product literature).

*A wide variety of microporous membrane materials exist. Teflon was chosen here for its high temperature properties.

11. Hercules Product Literature. *Magnamite AS4/3501-6*. Hercules Aerospace Products Group, July 1985.

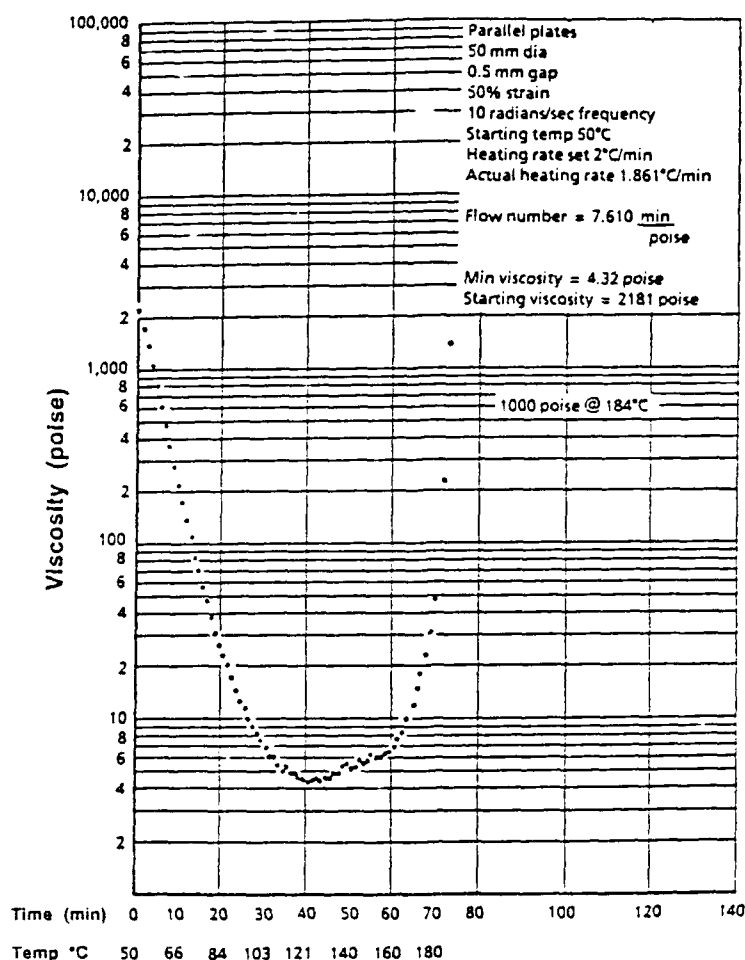


Figure 5. Dynamic viscosity of Hercules 3501-6 epoxy resin (from Hercules Fibers, Inc. product literature).

Thick Laminate Prepreg

TLP is the trade name of a product developed at Narmco Materials, Inc. It is reported to lower void levels in laminates by intentionally manufacturing the T300/5208 epoxy prepreg to a partially impregnated state.^{9,10} The proposed argument as to how it works is along the same lines as PSL. With the TLP partially impregnated, it is proposed that a porous network is setup throughout the preform volume. This allows entrapped gases to quickly exit the interior upon vacuum bagging.^{9,10} Upon further heating and subsequent resin flow, and application of autoclave pressure, the preform is said to complete its impregnation, leaving a void-free laminate.^{9,10} No special lay up procedures are required. This material was also tested in a vacuum bag process to evaluate its potential for nonautoclave processing.

Void Measurement

Carrying out this program properly entailed a detailed analysis of several destructive techniques for measuring voids in carbon/epoxy composites. Void content can be a difficult quantity to measure with confidence, even when measuring in a relative sense. It is quite difficult

to determine true void content;¹² this is in large part due to the fact that voids make up such a small percentage of the composite volume that their measurement is near the tolerance range of the methods used to measure them. For an indepth report of the void content measurement techniques used in this study, the reader should refer to Reference 12.

Two general types of destructive measurement methods were used: density determination/matrix digestion (DD/MD) and optical image analysis (IA). These two methods each applied two different techniques. The DD/MD method included both the water buoyancy technique (ASTM D 792) and the density gradient technique (ASTM D 1505). The IA method included two different optical image analysis systems: the Dapple IA system* and the Omnimet IA system.†

Past work on carbon/epoxy composites at this laboratory has shown that values for void content vary between methods.^{12,13} Void content determined from DD/MD methods are typically lower (even negative) compared to IA results due to tolerance errors introduced and propagated in the void content calculation.^{12,13}

These four void measurement techniques were applied to each process group. Each DD/MD technique was applied to the same specimen sets; each IA technique was also applied to the same set of separate specimens cut from the same laminates.

DD/MD Techniques

Two separate density determination methods were used on each CFRP specimen prior to matrix digestion. These were the water buoyancy technique (ASTM D 792) and the density gradient technique (ASTM D 1505, Method C).

- **Water Buoyancy Technique:** The density of each composite specimen was measured according to the ASTM standard. Through the known density of water, this technique gives a measurement of specimen density by two weighings: the specimen dry weight, then the buoyant weight of the same specimen suspended by a wire in a beaker of degassed distilled water. A laboratory balance with an accuracy of ± 0.0001 g was used for all dry and wet weighings. The water density was corrected for temperature.
- **Density Gradient Technique:** The density gradient technique measures specimen density directly; no calculations are used. This technique is more involved than the water buoyancy technique and provides more precise results.¹² Aqueous salt *heavy liquid* was chosen as the medium for density measurement. The density of the liquid medium is set by the amount of a complex salt dissolved into water. Liquid densities ranging from 1.0 g/cc to 2.5 g/cc could be made with these solutions. The apparatus includes a 70 cm glass column marked with antiparallax grids for accurate height measurement (± 0.5 mm), a plexiglass water jacket, and a circulating temperature control unit which maintained the water temperature in the jacket at $23^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. This apparatus kept the fluid gradient convectively stagnant and stable.

*Dapple Image Analyzer, Dapple Systems, Sunnyvale, CA.

†Omnimet II Image Analyzer, Buehler, Lake Bluff, IL.

12. GHIORSE, S. R. *A Comparison of Void Measurement Methods for Carbon/Epoxy Composites*. U. S. Army Materials Technology Laboratory, MTL TR 91-13, April 1991.

13. RICCA, J. J., JURTA, R. M., and DADY, C. Unpublished results. 1986.

A peristaltic pump fitted with a three-roller pump head sized for No. 14 Tygon tubing was used to fill the column. Five calibrated sink floats (± 0.0005 g/cc) were prewetted in a separate beaker of the light liquid solution and slowly immersed into the filled column with tweezers. Next, approximately 10 specimens were prewetted in the light solution and slowly immersed into the column. The floats and specimens were then left to settle for two hours. The column calibration line was determined by finding the least squares linear fit of the float standard density value versus height. Correlation coefficients were 0.995 or higher for all columns. Turbulence created by immersing the 15 objects into the column had a remarkably slight effect on gradient linearity and stability despite the fact that the specimens were 2.5 cm x 2.5 cm x 0.3 cm in size.

- **Matrix Digestion:** Once the two density tests were complete the specimen fiber weight was determined by matrix digestion (ASTM D 3171). The two epoxies used in this study were both suited to digestion in heated concentrated nitric acid. CFRP specimens weighing approximately two grams were placed in a 600 cc beaker containing 75 cc of concentrated nitric acid. The beaker was covered (but not sealed) and placed in a ventilated hood on a hotplate and heated to 80°C. After two hours the beaker was removed and the bare fibers rinsed with water. They were washed two rinses beyond the point where no sign of the reaction residue was visible to the eye. This was typically five rinses. The fibers were then thoroughly dried at 115°C for six hours and left to cool overnight. The next day the fiber weight was determined on the laboratory balance.

Control tests were run on the T300 and AS4 fibers to determine the correction factor, K_{fc} , for acid reactions with the carbon fibers. No correction was needed for the glass scrim fibers. In the control tests, bare carbon fibers were weighed and run through the same matrix digestion procedure as the composite specimens. After drying they were weighed again. The ratio of the final weight to the starting weight is the correction factor K_{fc} .

Once specimen density and fiber weight were known, specimen theoretical density, void, fiber, and matrix volume fractions were calculated by the following relations:

$$\rho_t = W_c / [(K_{fc} W_{fc} / \rho_{fc}) + (W_{fs} / \rho_{fs}) + (W_m / \rho_m)] \quad (1)$$

$$v_v = 1 - \rho_e / \rho_t \quad (2)$$

$$v_f = [(K_{fc} W_{fc} + W_{fs}) / W_c] / [\rho_e / (\rho_{fc} + \rho_{fs})] \quad (3)$$

$$v_m = (W_m / W_c) (\rho_e / \rho_m) \quad (4)$$

These calculations were done for each specimen using both the water buoyancy-determined and gradient column-determined experimental density data sets. The manufacturer quality assurance specifications for values of fiber and resin density were used in these calculations.

Optical Image Analysis

Since the void results were the focus of this study, several approaches to determining void content were taken: two variations of the matrix digestion method and two optical image analysis (IA) methods.

The two IA systems used to determine void content were the Dapple IA system and the Omnimet IA system. Both methods allowed quantitative, as well as qualitative inspection of the carbon/epoxy specimens.

- Specimen Preparation: Both IA methods used the same set of specimens for study. Approximately square specimens (2.5 cm x 2.5 cm) were cut from the central area of the test laminates for materiallographic preparation. These specimens were then cut in half at 45° to the 0/90 fiber directions and encapsulated in mounting epoxy for polishing. This cross-sectional angle eliminated fiber pullout during polishing. Also, the 45° orientation produced uniform optical contrast of the fibers for optimal IA measurement. Each specimen was measured a minimum of three times and the average void value recorded.
- Dapple Image Analysis: The Dapple IA system was used to measure the average void area fraction (which is equivalent to void volume fraction) of each specimen cross section.¹⁴

In the Dapple technique, the entire area of each polished cross section is first viewed qualitatively with a light microscope to observe the overall laminate. Four representative areas of the cross section surfaces were then chosen and photographed at 40X magnification. The actual sampling area was 4.5 mm² to 5.0 mm² per photograph. The total sampling area per specimen was 18 mm² to 20 mm². The photographs were then measured for void area fraction using the Dapple IA system, which calculated the average void area fraction over the entire photographic image. The Dapple IA system measures features of area acquired from video images. The hardware consists of a personal computer, TV camera, 9 inch TV monitor (for actual image observation), 12 inch monochrome high resolution monitor (for image processing and measurement), and conventional lighting apparatus. The accompanying software package digitizes and measures the video images. For each video image the brightness is measured in 64 gray level steps at each point in a 254 x 192 pixel array. The software allows the operator to separate the areas or features of interest from the background via gray level discrimination. These detected or discriminated areas can then be stored, reprocessed, measured, and statistically analyzed.

- Omnimet Image Analysis: The Omnimet Image Analyzer also discriminates and measures video images. However, this personal computer-based system is interfaced directly to an optical microscope via a Vidicon high resolution camera. This system offers increased magnification and allows for direct measurement of voids from polished specimens. The polished laminate cross sections were imaged and measured at 250X magnification via the optical microscope. The voids were discriminated and measured for each area viewed. Approximately 2 mm² of specimen area was measured for each specimen. This is an area 10 times smaller than that measured by the Dapple technique. The areas were measured through the entire thickness at 60 random points over the cross section. In addition to void area fraction, the Omnimet system can be used to measure fiber area fraction.

14. UNDERWOOD, E. E. *Quantitative Stereology*. Addison-Welsey, ed., 1970, p. 27.

RESULTS AND DISCUSSIONS

Vibration-Assisted Vacuum Composite Processing

The two DD/MD techniques used for determining composite density agreed closely (see Table 2). The gradient column data were more consistent while the water buoyancy data recorded higher scatter. VAVCP increased the laminate density on the order of 0.5%. This result corroborates the lower void content result. An increase in composite density would generally be expected to accompany the lower void content, and the density increase is likely due to void expellation; however, the actual case is more complex and calls for cautious interpretation of the test results. Resin content and fiber uniformity cannot be assumed to remain unchanged by VAVCP. These data are not precise enough to distinguish if part of the observed density rise was due to increased resin movement and/or more uniformly distributed fibers. With limited data a complete description of the density increase cannot be put forth.

Table 2. CARBON/EPOXY LAMINATE AVERAGE DENSITY OF STATIC VERSUS VIBRATORY PROCESSING (FOUR PROCESSING RERUNS)

	Spec Count	Water Buoyancy (g cm ⁻³ ± σ)	Density Column (g cm ⁻³ ± σ)
Static	22	1.538 ± 0.011	1.540 ± 0.011
Vibratory	28	1.559 ± 0.009	1.544 ± 0.008
% Change		+ 1.36	+ 0.25

In Table 3 the void content results are listed for each DD/MD and IA method. The overall agreement between methods is good. The average 54% decrease in void content using the vibration cure process versus the static cure process is a key finding. These data strongly suggest that the vibratory energy is providing or augmenting a mechanism for void migration through and out of the viscous preform. It is postulated the vibration is providing kinetic energy to the gas bubbles, enabling them to overcome potential energy barriers encountered during their movement out of the preform along lamina layers. This being the case, it stands to reason that an extended staging dwell will produce still lower void levels as the migration process is likely a slow, steady phenomena.

Table 3. AVERAGE VOID CONTENT OF STATIC VERSUS VIBRATORY PROCESSED CARBON/EPOXY LAMINATES (FOUR PROCESSING RERUNS)

	DD/MD			Image Analysis			
	Spec Count	Water Buoyancy (vol % ± σ)	Density Gradient Column (vol % ± σ)	Spec Count	Dapple (vol % ± σ)	Omnimet (vol % ± σ)	Average (vol %)
Static	22	2.7 ± 0.4	2.5 ± 0.3	8	2.8 ± 1.1	2.1 ± 0.8	2.5
Vibratory	28	1.4 ± 0.3	1.2 ± 0.2	8	1.2 ± 0.7	0.8 ± 0.5	1.2
% Change		- 48	- 52		- 57	- 62	- 54 ± 5

In Table 4 the average number of voids present and average void size in the cross sections in the IA specimens are listed for both process groups. These data were determined using the Omnimet IA technique. The 59% decrease in the void count agrees with the measured 54% decrease in overall void content. An interesting result here is the measured 10% increase in average void size when VAVCP was used. This may indicate that the vibration causes increased coalescing of smaller voids during their migration through the laminate. Shukla, et al., observed a similar phenomena in vibrated molten aluminum.¹⁵

Tests on larger structures, woven structures, contoured structures, and structures using higher viscosity resin systems are needed to define the void reduction limitations of VAVCP observed in this study. A high payoff of this process would be in vacuum fabrication of large-scale structures where low void content is required to maintain high quality. Vacuum bagging large-scale composite structures, and applying mechanical vibration during the cure cycle may result in improved quality to the point where the economical vacuum bag process can be used in place of the autoclave. VAVCP may also be useful in autoclave processing of resin systems high in volatiles, such as polyimides. Further void sizing study, coupled with mechanical property testing, are necessary to determine if the suspected void coalescing phenomena actually occurs, and if so, to what degree it effects net short- and long-term mechanical performance.

Table 4. NUMBER AND SIZE OF VOIDS IN STATIC VERSUS VIBRATORY PROCESSED CARBON/EPOXY LAMINATE CROSS SECTIONS DETERMINED USING THE OMNIMET IA TECHNIQUE (FOUR PROCESSING RERUNS)

	Spec Count	Average Number of Voids	Average Void Size (μm^2)
Static	8	112	2730
Vibratory	8	45	2990
% Change		- 59	+10

Porous Scrim Layering

Figure 6 shows a schematic of the proposed gas removal scheme central to successful PSL. All scrims necessarily remain a permanent part of the cured laminate after processing. Preliminary screening was done on a variety of scrim types: nonwoven carbon mat, open mesh style 1643 glass, style 104 plain woven glass, and style 3733 plain woven glass. The screening tests identified style 104 plain woven glass as the most viable porous scrim layer for the prepreg used in this study. The nonwoven carbon mat formed an excellent porous layer, however, its fiber content was too low (10%) leaving an unacceptable resinous layer within the laminate.

15. SHUKLA, D. P., GOEL, D. B., and PANDEY, P. C. *Effect of Vibration on the Formation of Aluminum Alloy Ingots*. Metl. Trans. B., v. 11B, 1980, p. 166.

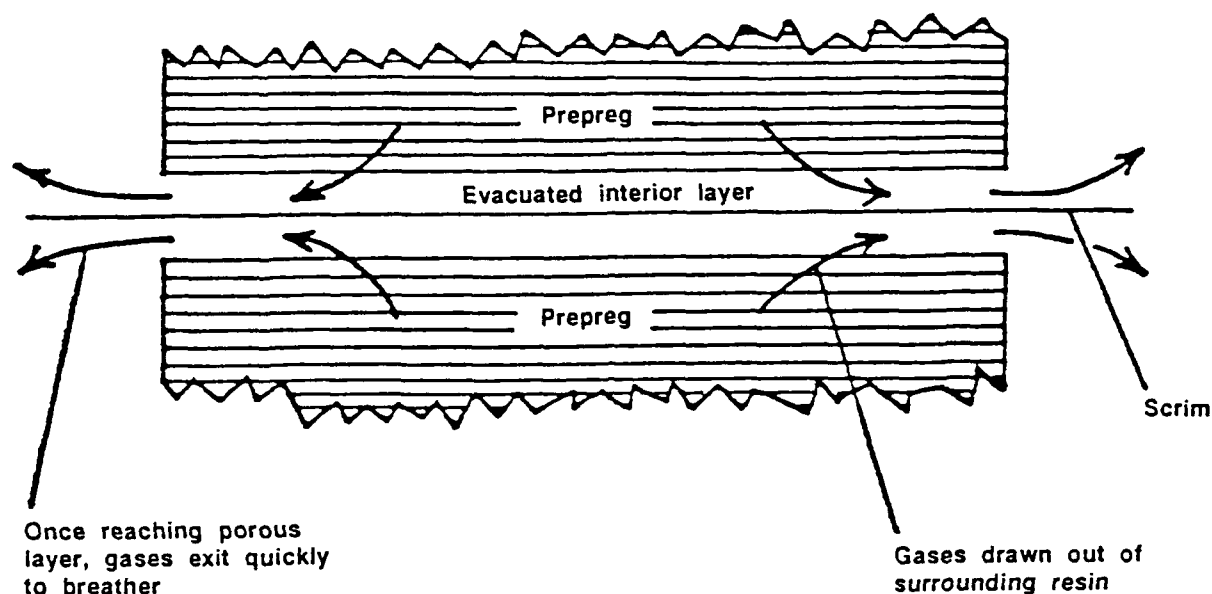


Figure 6. Schematic of proposed porous scrim laying gas removal mechanism.

In the second round of PSL tests, the style 104 plain woven glass scrim was used and varied from one to four layers in the various test laminates. The void content results are shown in Table 5. The PSL process had little, if any, effect on void content. PSL appears to be ineffective in removing established void bubbles, such as those mechanically entrapped during lay up. Established voids in nearby layers did not make the vertical migration to the evacuated scrim layer. Resistance to void movement in the vertical direction is extremely high and this result was not totally unexpected. Dissolved diffusing gas was, however, expected to make its way to the scrim layer but apparently did not. It appears from the data and photos that the areas immediately adjacent to the scrim were the only locations cleared of voids and that the porous scrim layer had negligible effect on overall void content. The reasons for failure of the PSL process are not entirely clear, but two phenomena are proposed as causes. First, the particular Hercules AS4/3501-6 prepreg batch used in this study may have been quite low in volatiles, leaving no void effect to be studied. Evidence in support of the *low volatiles* assumption was found in the MMP testing (see below). Another possibility is that upon heating, resin flowed quickly to seal the porous pathway. This, however, is unlikely based upon the positive findings observed using TLP which works on a similar gas removal scheme as PSL (see below).

Table 5. EFFECT OF STYLE 104 E-GLASS POROUS SCRIM LAYERING ON THE VOID CONTENT OF VACUUM BAGGED CARBON/EPOXY LAMINATES

Plate	Center Scrim Layer	Spec Count	Void Volume Fraction				Average (%)
			WBT (%)	DGT (%)	Dapple (%)	Omnimet (%)	
S1	Control	6	2.4	1.7	1.7	1.8	1.9
S2	104 x 1	6	1.9	1.8	2.0	1.9	1.9
S3	104 x 2	4	2.8	2.7	2.7	2.1	2.6
S4	104 x 3	6	3.2	3.3	2.2	2.0	2.7
S5	104 x 4	6	2.4	2.4	4.5	2.4	2.9

Microporous Membrane Processing

Tests run using MMP in this study did not fully confirm previous results reported by Matienzo, et al.² and Newsam.³ Figure 7 shows a schematic of the proposed mechanism for successful MMP. The results, as shown in Table 6, indicate that the control laminate had the lowest void content while all others, except for the one hour 120°C staging dwell, were significantly higher in void content. Resin viscosity remained low for about six hours (see Figure 4). Diffusing gases should have had ample time to exit the preform prior to gelation. One explanation is that, like PSL, MMP is effective in removing only dissolved gases from the liquid resin. Entrapped established voids, though exposed to the pressure gradient, encounter far too much resistance to migrate vertically. Deflation of these established voids by gas diffusion across the void/resin interface apparently did not occur. It is suspected that the batch of Hercules prepreg used in this study had minimal dissolved volatile gas and that its porosity was caused almost wholly by mechanical entrapment of air during lay up. The membrane, like the porous scrim layer, are thought to be ineffective in removing mechanically trapped gas.

Another test was run to find evidence of gas removal by diffusion through the membrane. The prepreg was exposed to moist air for a period of 24 hours (50% relative humidity at 22°C). Next, four (0/90)_{2s} two-inch-square preforms were laid up and vacuum bagged onto a release-coated Pyrex glass plate. A microporous membrane was placed over two of the preforms while the other two were covered by a solid barrier nylon film. All four preforms were then heated on a hotplate. As the temperature increased, profuse and, for a time, violent outgassing was observed around the perimeter of the solid barrier film preforms. The MMP preforms also outgassed around their perimeter, but to a dramatically lighter extent. These results lead to the conclusions that this Hercules prepreg batch was low in dissolved volatiles, and that the MMP is able to remove dissolved volatiles.

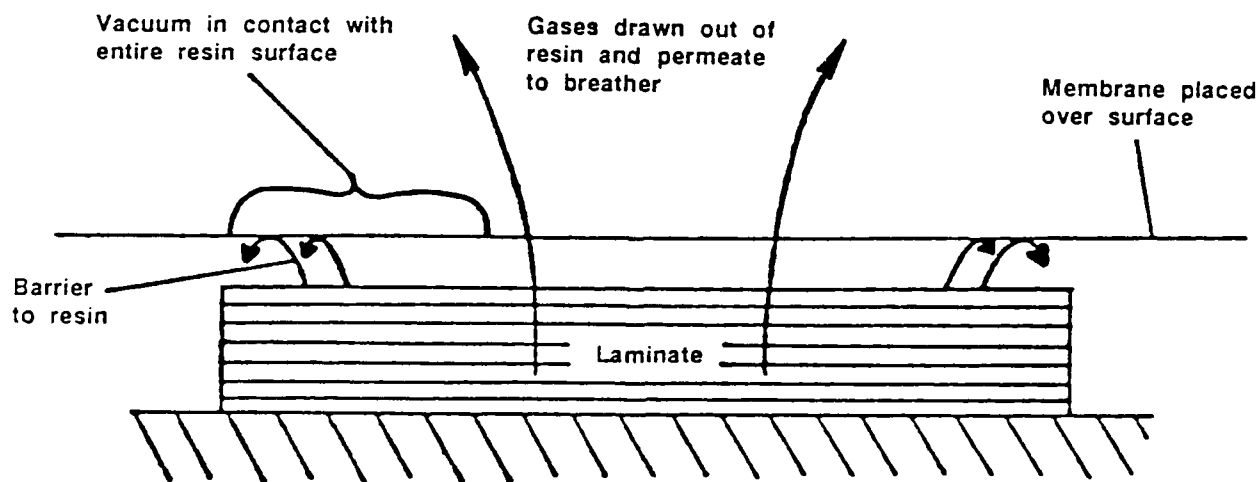


Figure 7. Schematic of microporous membrane processing gas removal mechanism.

Table 6. EFFECT OF MICROPOROUS MEMBRANE PROCESSING ON THE VOID CONTENT OF VACUUM BAGGED CARBON/EPOXY LAMINATES

Plate	120°C Degas Dwell (Hrs)	Spec Count	Void Volume Fraction				Average (%)
			WBT (%)	DGT (%)	Dapple (%)	Omnimet (%)	
M1	Control	5	2.4	1.7	1.7	1.8	1.9
M2	1/2	5	2.2	2.2	5.8	5.2	3.9
M3	1	5	1.8	1.8	2.4	1.9	2.0
M4	2	6	2.5	2.7	3.6	3.2	3.0
M5	4	5	3.0	3.1	6.4	4.9	4.4
M6	6	6	3.0	3.4	4.4	4.8	3.9

Thick Laminate Prepreg

The effectiveness of Narmco's T300/5208 epoxy resin TLP in reducing void content in autoclave processed laminates was not determined by these tests. The TLP was tested in both autoclave and vacuum bag processing (see Table 7). In the autoclave test group no voids were found; however, the control laminate was also void free. When a 150 ply TLP preform was processed in the autoclave only trace amounts of voids were observed. Again, a 150 ply autoclave processed T300/5208 control laminate recorded only slightly higher porosity levels. This testing did confirm the fact that TLP, even though not fully impregnated at the start of processing, had no detrimental effect on the final composite.

Table 7. EFFECT OF NARMCO THICK LAMINATE PREPREG ON THE VOID CONTENT OF VACUUM BAGGED AND AUTOCLAVED CARBON/EPOXY LAMINATES

Plate	5208 Epoxy Laminate Cure	Spec Count	Void Volume Fraction				Average (%)
			WBT (%)	DGT (%)	Dapple (%)	Omnimet (%)	
Vacuum Bag Cycle							
T1	Control	5	- 0.5	0.2	2.0	1.9	0.9
T2	TLP	5	0.8	- 0.9	0.0	0.0	- 0.4
Autoclave Cycle							
T3	Control	6	- 0.4	- 0.3	0.0	0.0	- 0.2
T4	TLP	4	- 0.7	- 0.5	0.0	0.0	- 0.3
T5	Control, Thick*	4	0.3	0.2	0.0	0.0	0.1
T6	TLP, Thick*	4	0.2	0.2	0.0	0.0	0.1

*(0/90)₇₅ Lay up, 3/4 inch thick.

In vacuum bag testing the TLP lowered void content from approximately 2% to 1% in the cured laminate; an encouraging reduction of 50%. Although the TLP was not intended for use in vacuum bag processing, it nevertheless did act to lower void content significantly. In light of the results obtained from the other processes investigated in this study, it is not clear by what means the TLP achieved void reduction. The TLP uses Narmco's 5208 epoxy resin while all the other process test groups used Hercules' 3501-6 epoxy resin. As with the

PSL and MMP processes, the TLP process provides a means for volatiles to quickly exit the preform interior. Established voids, as previously discussed, are another matter. Their movement is restricted to two-dimensional migration along the lamina planes. However, a fundamental difference exists between the TLP process and PSL or MMP. This difference possibly makes TLP effective in removing established voids as well as volatiles. In the PSL and MMP processes, bubbles are required to follow a tortuous path in order to reach the porous site; however, the porous sites within a TLP preform are distributed throughout its volume. It is, therefore, plausible that the TLP is able to accomplish void reduction by both means: by providing a porous pathway for volatiles to quickly exit the laminate, and also by making this porous pathway in the form of a quasi-continuous network where gas bubbles need only migrate short distances to reach a porous site. Impregnation of the TLP preform was fully completed without the addition of autoclave pressure. Based upon these test results TLP would be a useful and cost effective means of reducing void content in vacuum bag processing applications.

SUMMARY

The results of this study revealed some effects of applying low frequency vibration during vacuum bag processing of polymer composite laminates (VAVCP). The addition of VAVCP during the pregelation period of the carbon/epoxy, 0/90 cross-ply, prepreg laminate cure cycle markedly decreased void content from 2.5% to 1.2%; a reduction greater than 50% over the static cure control group. Under the postulated mechanism, void removal by vibrating the preform is accomplished by supplying migrating-established gas bubbles with the needed kinetic energy to overcome potential energy barriers encountered as they move along lamina planes. It is reasonable to expect that an extended staging dwell will lower void content still further as long as the resin viscosity remains low at the staging temperature.

The data indicates that increased void size (likely due to coalescence) is another effect of VAVCP, even though overall void content decreased sharply. This speculation requires additional analysis to verify the occurrence of the phenomena and the net effect of VAVCP on mechanical performance.

VAVCP increased the carbon/epoxy laminate density from 1.541 g/cc to 1.545 g/cc; an increase on the order of 0.8%. Although it is likely that this is largely a result of the decreased void content, the added variables of fiber and resin movement mask the degree to which lower void content played a role in the composite densification.

The porous scrim layering process had no detectable effect on void content in the carbon/epoxy laminates. The reason for this is not clear, but two phenomena are proposed as causes. First, the prepreg batch in this study is thought to have been unusually low in volatile water vapor, which left no void effect to be detected. This conjecture is supported by the MMP and TLP test results. Future testing using PSL on moistened prepreg is needed to study its effectiveness on removing volatile vapors. Another possibility is that, upon heating, resin flowed quickly to seal the porous pathway. This, however, is unlikely based upon the positive findings seen using Narmco's TLP, which works on the same principle as PSL. PSL was ineffective in removing established gas bubbles.

Microporous membrane processing was ineffective in removal of established gas bubbles. These bubbles were unable to move orthogonal to the lamina planes due to extreme resistance to motion in that direction. Deflation of these established bubbles by gas diffusion

across the bubble/resin interface was not detected. Testing on moistened Hercules AS4/3501-6 epoxy prepreg showed that the membrane is able to remove volatile water vapor from within the laminate.

The autoclave processed Narmco T300/5208 epoxy TLP results were inconclusive due to a lack of a *void problem* to study in the control group itself. However, when used in vacuum bag processing the TLP proved to be an effective void reduction processing, lowering the void content from approximately 2% to 1%; a 50% decrease.

Based upon the results of this study, hybrid vacuum bag techniques combining any or all of the VAVCP, MMP, and Narmco TLP processes, and also an extended low temperature staging dwell, have high potential for producing a low void, high quality vacuum bag processed laminate. MMP and TLP would work to lower voids arising from dissolved volatile gas sources, while the VAVCP, and also the TLP, would work to remove established gas bubbles.

More needs to be learned about the behavior of voids in the interior of curing composites. A particularly productive next step would be to develop a computer simulation of void behavior within composite preforms to go along with gathered experimental data. Having a theoretical model available to compliment experimental data will allow manipulation of numerous parameters which come into play in this complex combination of physical phenomena; e.g., resin viscosity and volatiles, fiber content and weave, and vibration frequency and amplitude. In this way, a faster convergence on understanding the underlying mechanisms and optimizing specific hybrid combinations of VAVCP, MMP, TLP, and staging dwells would be realized.

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